

(11) (A) No. **1 136 384**

(45) ISSUED 821130

(52) CLASS 23-348

³
(51) INT. CL. B01D 53/14, 53/34

(19) (CA) **CANADIAN PATENT** (12)

(54) REGENERATION OF SPENT SO_2 - SO_3 SORBENTS
WITH H_2S AT MODERATE TEMPERATURE

(72) Longo, John M.;
Cahn, Robert P.;
Steger, John J.,
U.S.A.

(73) Granted to Exxon Research and Engineering Company
U.S.A.

(21) APPLICATION No. 339,103

(22) FILED 791102

(30) PRIORITY DATE U.S.A. (957,557) 781103

No. OF CLAIMS 6 - NO DRAWING

BRIEF DISCLOSURE

10 The metal oxides CeO_2 , either supported or unsupported,
used to remove sulfur oxides from waste gas effluent streams by
conversion into cerium sulfate and/or cerium oxysulfate, is re-
generated to the starting cerium oxide by means of a reducing
regenerating atmosphere consisting essentially of H_2S as the re-
ducing component at a concentration of from 0.5 to 100 vol. %,
preferably 1-70 vol. %, most preferably 5-70 vol. %, the balance
comprising non-regenerating non-reactive and inert gases such as
helium, argon, CO_2 , nitrogen, water vapor, etc. at a temperature
of from 300-700°C, preferably 350-700°C, most preferably 450-600°C
in the presence of sufficient oxygen to convert any SO_2 in said
gas to SO_3 , (in the SO_2 removal step) the reducing-regenerating
atmosphere passing at any convenient rate, such as from 50 to
50,000 V/V/Hr, preferably 100 to 50,000 V/V/Hr, most preferably
100-20,000 V/V/Hr.

20 Regeneration is typically conducted on the cerium oxide
sorbent which has been converted to cerium sulfate, and/or oxy-
sulfate to the extent of 10 to 100 mole %, preferably 10-70 mole %.
Regeneration of the cerium-sulfur oxide compounds to the cerium
oxide is accompanied by the liberation of SO_2 which is conveniently
used with additional H_2S in a Claus plant for conversion to ele-
mental sulfur.

DISCLOSURE

Metal oxides selected from the group consisting of CeO_2 ,
copper oxides, iron oxides, preferably CeO_2 , either supported or
unsupported, which have been used as a sorbent to scrub sulfur
oxides (i.e. SO_2 , SO_3 , etc.) from waste gas effluent streams and are

1136384

th reby conver' d to the metal sulfate, and/or metal oxysulfate
(for use of CeO_2 see U.S. Patent 4,001,375).

are regenerated to the metal oxide by means of a reducing regenerating atmosphere consisting essentially of H_2S as the reducing-regenerating component present at from 0.5 to 100 vol. %, most preferably 5 - 70 vol. %, the balance comprising nonregenerating inert gases such as helium, neon, argon, CO_2 , nitrogen, water vapor, etc. and mixtures thereof, at a temperature from 300-700°C, preferably 350-700°C, most preferably 450-600°C, the reducing-regenerating atmosphere stream passing through the sorbent at any convenient rate, such as from 50 to 50,000 V/V/Hr, preferably 100 to 50,000 V/V/Hr., most preferably 100 to 20,000 V/V/Hr. This regeneration procedure can be practiced on either a cyclic or continuous basis.

The regeneration procedure of the instant invention is utilized in flue gas desulfurization processes in which the flue gas is contacted with a sorbent comprising cerium oxide in either the +3 or the +4 oxidation state. Preferably, the cerium oxide is supported on an inert support. The support is preferably an inorganic refractory oxide, for example, various aluminas, silica, etc. The support can be of various shapes, such as pellets, extrudates, Raschig rings, saddles or monoliths, e.g. honeycombs. The most preferred support is γ -alumina, especially in the shape of Raschig rings.

The support will have a surface area of from 10 m²/g to 300 m²/g, preferably from 100 m²/g to 200 m²/g. The cerium oxide is combined with the support at from 1 to 40 wt. % of said support. Preferably, the sorbent will comprise from 2 to 20 wt. % cerium oxide.

In the following discussion CeO_2 will be used as the specific example, it being understood that equivalent arguments and descriptions are available and operable for other

metal oxide sorbents unless specifically indicated otherwise. The supported cerium oxide sorbent may be prepared by methods known in the art for preparing supported catalysts for use in petroleum processes, e.g. reforming, hydrocracking, etc. For example, an aqueous solution of a cerium oxide precursor may be impregnated onto an alumina support. The impregnated support may be subsequently separated from excess solution, dried at a temperature of from about 20° to 110°C and calcined at a temperature of from about 300°C to 600°C . During the drying and/or the calcining step, the supported catalyst may be contacted with air or O_2 to convert the cerium oxide precursor compound on the support into the oxide.

An alternative approach to the preparation of a cerium oxide impregnated support which places the CeO_2 on the outer surface of a porous support involves prefilling of the pores with an inert liquid as described in U.S. Patent 2,746,936,

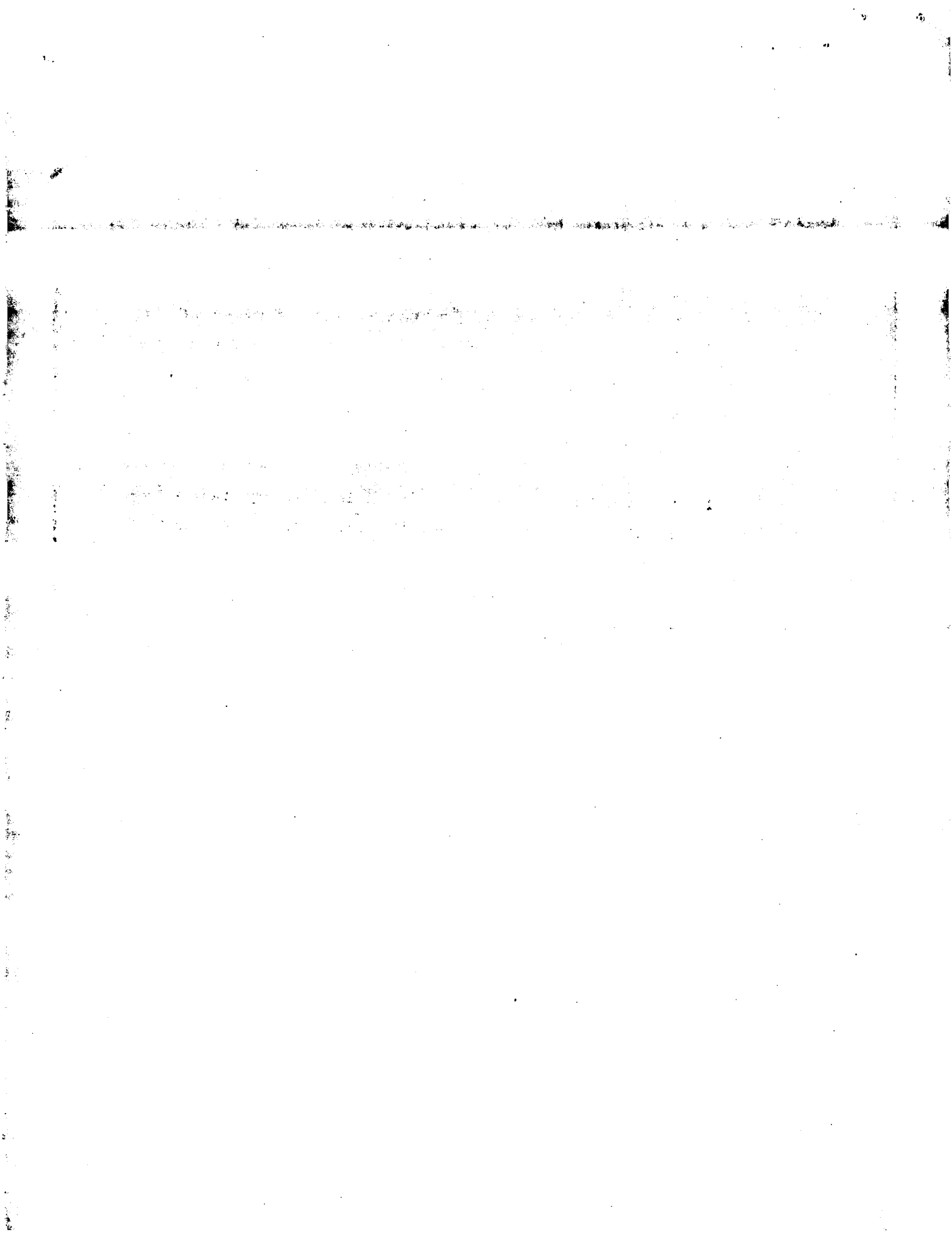
For convenience, the catalyst is impregnated with an aqueous solution of the cerium oxide precursor. However, organic solvents may be utilized provided the cerium oxide precursor is soluble therein. Precursors of the preferred sorbent, cerium oxide, which are soluble in aqueous solutions, include ceric ammonium nitrate, cerous nitrate, basic ceric nitrate, cerous acetate, etc. For other metal oxides, similar metal salts may be utilized.

The waste gas effluent stream scrubbed is typically a

B

1 gas, preferably a flue gas, which comprises from 0.01 to 2.0%
2 by volume (100 ppm to 20,000 ppm) sulfur oxides. This waste
3 gas stream is contacted with the sorbent described above.
4 Additionally, the waste gas stream contains O_2 sufficient to
5 convert all SO_2 to SO_3 and may also comprise N_2 , CO_2 , CO , H_2O ,
6 NO_x , etc. It should be noted that none of these additional
7 components will interfere with the scrubbing of the gas stream.
8 In practice, at least a stoichiometric quantity of oxygen in the
9 waste gas is needed to permit the absorption of SO_2 on CeO_2
10 to form the sulfate or oxysulfate. During the initial contacting
11 step, the temperature is maintained at from $300^\circ C$ to $700^\circ C$,
12 most preferably from $450^\circ C$ to $600^\circ C$. The pressure is not
13 critical. For convenience, whatever pressure is obtained at
14 the flow and temperatures utilized will be acceptable. The
15 flow of the flue gas through the initial contacting zone, i.e.
16 the zone in which the sorbent is contained, may vary from 50
17 to 50,000, preferably from 500 to 50,000, and most preferably
18 from 500-20,000 V/V/Hr. In the initial contacting zone, the
19 catalyst may be present in the form of pellets, extrudates,
20 etc. After a certain time, depending on the above contacting
21 conditions, the cerium oxide will be converted substantially
22 to cerium sulfate and/or cerium oxysulfate.

23 When the conversion of the cerium
24 oxide to the corresponding sulfate or oxysulfate reaches from 10-
25 100%, preferably 10-70% of capacity, the sorbent is regenerated
26 by the process of the instant invention utilizing an H_2S con-
27 taining gas wherein the reducing-regenerating agent consists
28 essentially of the H_2S present at a concentration of from 0.5
29 to 100 vol. %, preferably, 1-70 vol. %, most preferably 5-



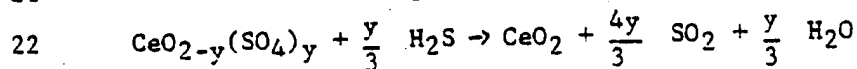
1 70 v l. %, the balance of the stream being nonregenerative,
 2 nonreactive inert gas such as nitrogen, helium, argon, neon,
 3 water vapor, CO₂, etc. The cerium sulfate, and/or oxysulfate
 4 is converted substantially to cerium oxide while the sulfur
 5 is removed as sulfur dioxide from the sorbent.

6 When dealing with the cerium-system for example,
 7 if reaction of the spent cerium sorbent with H₂S goes too far
 8 and begins to convert the regenerated cerium oxide to the
 9 sulfide, a treatment with air, air/steam mixture, or steam
 10 alone can be used to restore the sorbent to full capacity.
 11 Preferably the atmosphere is steam. The temperature at which
 12 this final step is performed (if it is necessary) ranges from
 13 300-700°C, preferably, 400-700°C, most preferably 450 to 600°C.
 14 This step converts any sulfide back to the oxide with only
 15 small amounts of sulfate formation. The reaction of cerium
 16 sulfide with oxygen to give almost quantitatively the oxide
 17 is unique for cerium among the lanthanide sulfides which
 18 generally burn to give oxysulfates.

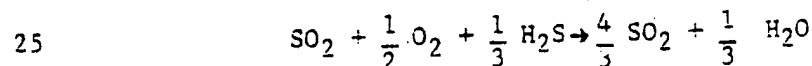
19 Cerium oxysulfates have the general formula:

20 $CeO_{2-y}(SO_4)_y$ where $0 < y \leq 2$.

21 The overall general regeneration reaction is:

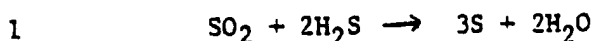


23 so that the overall method is to sequester SO₂ from a flue
 24 gas and recover it as concentrated SO₂ as follows;



26 Any SO₃ present in the flue gas will also be removed.

27 The SO₂ thus formed can be reacted with additional
 28 H₂S over the amount needed to regenerate the sorbent to form
 29 elemental sulfur by the Claus reaction:



2 which can be made to proceed in the same or a separate
3 reactor from the CaO_2 containing vessel. Note that a mole
4 of H_2S is able to reduce three times as much sulfate as a
5 mole of hydrogen, a major advantage of this method of regen-
6 eration over the prior art.

7 Alternatively, the SO_2 thus formed may then be fed
8 to a separate Claus plant for conversion to elemental sulfur.
9 In the Claus plant H_2S is mixed with the SO_2 to bring the
10 $\text{H}_2\text{S}:\text{SO}_2$ mole ratio to 2:1 prior to the catalytic converter.

11 One advantageous method of regenerating the spent
12 metal oxide sorbent is to pass an excess of H_2S -containing
13 gas over it, that is, in an amount in excess of the volume
14 of H_2S needed to just regenerate the sorbent so that $\text{H}_2\text{S}/\text{SO}_2$
15 mixture is produced, which can be fed directly to the Claus
16 plant. Indeed, some of the $2\text{H}_2\text{S} + \text{SO}_2$ Claus reaction takes
17 place over the metal oxide sorbent resulting in the production
18 of some elemental sulfur in the sorbent vessel.

19 As previously stated, this regeneration procedure
20 can be practiced in either a cyclic or continuous manner.
21 When operated in a cyclic manner the scrubber-regenerator
22 comprises multibed units, wherein a gas mixture containing
23 sulfur oxides is passed through one or more fixed beds of sup-
24 ported cerium oxide. While these beds are scrubbing sulfur
25 oxides, the other beds of the unit are being regenerated with
26 an H_2S containing gas as described. The roles of the scrubber
27 and regenerator are reversed when both have completed their
28 task. Purging with a gas stream such as steam, between these
29 two steps may be advantageous both to prevent explosive conditions

as well as for converting any cerium sulfide which may have formed in the regeneration step to cerium oxide.

In another embodiment of the instant invention, the catalyst is continuously removed and regenerated. For example, see the apparatus described in U.S. Patent No. 3,989,798.

As stated above, the cerium oxide is preferably supported on an inert support material to most economically use the cerium oxide. However, unsupported cerium oxide may be used provided adequate surface areas are obtained. Preferably the unsupported cerium oxide should have a surface area of at least 10 m²/g, preferably from 20 m²/g to 50 m²/g. Such unsupported cerium oxide is regenerated by the same H₂S procedure as is supported cerium oxide.

EXAMPLES

A 5.5 g (8.2 cc) sample of 20% CeO₂ supported on extruded γ -Al₂O₃ is held in place by quartz wool within a vertical quartz tube (~1" dia.). A gas blend containing 3700 ppm SO₂, 5% O₂ and balance Ar is passed upward through the heated sample at 4000-5000 V/V/Hr. during the SO₂ scrubbing mode. The SO₂ content of the exit gas is analyzed using an electrochemical method containing a Faristor which is calibrated to read 100% at 5000 ppm SO₂. During regeneration, a 1% H₂S in He regeneration gas is run through the bed at ~1000 V/V/hr and the exit gas is bubbled through Pb(NO₃)₂ solutions. A white precipitate (PbSO₃) indicates SO₂ while a black precipitate (PbS) indicates H₂S in the gas stream and signals the end of a regeneration.

A number of SO₂ scrubblings, H₂S regenerations,

1 and optional burns were carried out under
2 the conditions described above. Typically, during the SO₂
3 scrubbing, the SO₂ content in the exit gas as a function of
4 time was as follows: 500 ppm/20 min; 1000 ppm/40 min; 1500 ppm/
5 65 min; and 2000 ppm/95 min. The regeneration at 500-600°C with
6 1% H₂S He took about 1 hr. before breakthrough of H₂S. The for-
7 mation of cerium oxysulfate, oxide, and sulfide were all moni-
8 tored by removing a small sample of extrudate at appropriate
9 times and examining the product by X-ray diffraction.
10 When a dry or wet H₂S containing gas is used for the regen-
11 eration, prolonged treatment of the spent sorbent may first
12 convert it to the oxide, followed by further conversion to
13 the sulfide, CeS₂. It was also shown that the resultant sul-
14 fide can be converted back to the oxide by passing an oxygen
15 and/or steam containing gas over it at 300-700°C.

16 The present invention is particularly well suited
17 for the removal of SO₂ from gases in an installation where
18 stoichiometrically adequate amounts of H₂S are also available
19 from other operations. Typical examples are as follows:

- 20 (a) Claus plant tail gas cleanup.
- 21 (b) SO₂/SO₃ removal from refinery flue gases.
- 22 (c) SO₂/SO₃ removal from flue gases in coal gasi-
23 fication or liquefaction plant, tar sand refineries, and the
24 like where H₂S is available as a byproduct.

" " "

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for desulfurizing an effluent waste gas stream comprising adsorbing sulfur oxides by a cerium oxide sorbent, at a temperature of from 300-700°C., in the presence of sufficient oxygen to convert any SO_2 in said gas to SO_3 and thereafter regenerating the spent cerium oxide sorbent, said process characterized in that said spent cerium oxide sorbent is regenerated by contacting said spent cerium oxide sorbent with an H_2S containing reducing-regenerating gas comprising from 0.5 to 100.0 volume percent H_2S with the balance comprising a non-regenerating gas, at a temperature of from 300-700°C. at a convenient flow rate.
2. The process of claim 1 wherein the H_2S containing reducing-regenerating gas flow rate ranges from 50 to 50,000 V/V/Hr.
3. A process according to claim 2 wherein the H_2S concentration in said reducing-regenerating gas ranges from about 1-70 volume percent.
4. A process according to claim 3 wherein said non-regenerating gas is helium, CO_2 , N_2 , Ar, water vapor or mixtures thereof.
5. The process of claim 4 wherein said cerium oxide is exposed, as a final regeneration step, to steam, air or steam/air mixtures to convert any CeS_2 to CeO_2 and wherein said exposure is conducted at a temperature of from 300-700°C.

1136384

6. A process according to any of one of claims 4 or 5 wherein said cerium oxide sorbent is supported on an inert support.

